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Analysing oily wastes in soils

Frédéric Coulon discusses a new method which should ease the pain of risk assessments of contaminated soils

Many hydrocarbon contaminated sites posing potential risks to human health harbour weathered, 'mid-distillate' or heavy oils. Now, a bioremediation consortium (PROMISE), led by Cranfield University, has developed a novel and robust analytical procedure for weathered hydrocarbon contaminated soils within a UK risk-based framework

Petroleum hydrocarbons are common environmental contaminants. They are components of crude oil, and products derived from it and are consequently found on a variety of sites including refineries, chemical materials and by products storage sites and manufactured gas production sites. They may also be present as a result of spills and leaks during transportation.

They are a highly complex mixture of aliphatic and aromatic hydrocarbons with minor amounts of other heterogenic compounds such as nitrogen, sulphur and oxygen. Once released to the environment, they are subject to physical, chemical and biological processes that further change their composition, toxicity, availability and distribution (partitioning) within the environment. Such degradation processes (weathering processes) include adsorption, volatilisation, dissolution, biotransformation, photolysis, oxidation, and hydrolysis.

Weathering

The extent of weathering experienced is particularly important when characterising petroleum contamination prior to remediation, especially the heavy oils, which have high viscosity (ca 50–360 mPa s), high boiling point (ca 300 to >600 °C) and carbon number ranges in excess of C20. These weathering processes shift their chemical composition towards recalcitrant, asphaltenic products of increased hydrophobicity.

Typical concentration of total petroleum hydrocarbons (TPH), ranging from C12 to C40, of weathered hydrocarbons is below 10,000 mg/kg. Volatile compounds such as benzene, toluene, ethylbenzene, xylenes (BTEX) are not detected or are less than 1 ppm, and the chloride concentration is less than 250

mg/kg. The aliphatic and aromatic fractions of weathered oils are usually ranging from C12 to C40 (see Table 1) These fractions are commonly less bioavailable within the soil due to their physico-chemical properties (eg solubility, volatility and K_{ow} water/octanol partitioning coefficient) which restricts further microbial attack and degradation.

However, attempts to improve the bioavailability of the aliphatic and aromatic fractions of weathered hydrocarbons to microorganisms during bioremediation activities may result in increased human exposure. These residual fractions are the principal source of the organic carcinogens or suspected carcinogens that drive quantitative risk assessment at contaminated sites.

Aliphatic fraction	Avg EC	Aromatic fraction	Avg EC
EC >5–6	5.5	EC >5–7	6.5
EC >6–8	7.0	EC >7–8	7.5
EC >8–10	9.0	EC >8–10	9.0
EC >10–12	11	EC >10–12	11
EC >12–16	14	**EC >12–16**	14
EC >16–35	25.5	**EC >16–21**	18.5
EC >35–44	39.5	**EC >21–35**	28.5
		EC >35–44	39.5
EC >44-70			57

Table 1: Petroleum hydrocarbon fractions (based on equivalent carbon number*) for use in UK human health risk assessment. Hydrocarbon fractions usually identified for weathered oils are in bold. * *The equivalent carbon (EC) number of a hydrocarbon is related to its boiling point (bp) normalised to the bp of an n-alkane series, or its retention time on a non-polar bp gas chromatographic (GC) column. For hydrocarbons where the boiling points are known, an EC can be calculated. Hexane contains six carbon atoms and has a boiling point of 69°C and an EC number of 6. Benzene also contains 6 carbon atoms and has a boiling point of 80°C. Based on benzene's bp and its retention time on a bp GC column, its EC number is 6.5. This approach has been recognised as a more appropriate differentiation technique than the actual carbon number of the chemical. For hydrocarbons with higher relative carbon number indices, the disparity (in terms of EC) between aliphatic and aromatic hydrocarbons is substantial.*

Too complex for risk assessment?

Although these important qualitative and quantitative differences between weathered and non-weathered

petroleum hydrocarbons are widely acknowledged, weathered hydrocarbons are not sufficiently understood or appropriately characterized for assessing risk at contaminated sites.

Measuring the total concentration of petroleum hydrocarbons (TPH) in soil does not give a useful basis for the evaluation of the potential risks to human and the environment. The variety of physicochemical properties, and thus differences in the migration and fate of individual compounds, and the toxicity of different fractions and compounds in oil products, must be taken into account in human health risk assessments.

Weathered TPH analysis in soil

There is a range of methods available for the analysis of weathered TPHs, including gravimetric analysis, infrared spectrometry (IR), gas chromatography with flame ionisation detector (GC-FID) and gas chromatography coupled to mass spectrometry (GC-MS). However, method choice may partially be restricted or influenced by economics and the risk assessment used during the remediation of contaminated land.

Many risk assessments now used during the remediation of contaminated sites incorporate analytical guidance and reference methods, but variations in protocols between frameworks may affect the remedial goals set. Indeed, the comparison of reference analytical methods used for petroleum risk assessment protocols highlights the need for more practical and simple extraction procedures that allow a better characterisation of both aliphatic and aromatic hydrocarbon fractions within oil-contaminated samples, including soil and sediment samples with high moisture levels.

In addition, concerns exist over the performance of current reference methods, specifically in terms of poor extraction efficiencies and analytical losses imparted by sample handling. Chemical composition may also alter over time, which may affect the accuracy of final measurements and lead to misrepresentations of human health risk.

To date, while the UK approach sets out guidelines for evaluating human health risks from petroleum hydrocarbon contaminated soils, as yet there has been no specification or adoption of recommended analytical procedures for these contaminants.

Furthermore, the framework itself notes that currently-adopted methods for petroleum hydrocarbon analysis may not be suitable for the heavier compounds, and questions whether it is practical or relevant for analysing weathered hydrocarbons.

Developing better analysis

These observations further highlight the need to develop a suitable and robust analytical procedure to

inform risk assessment which must be capable of analysing petroleum hydrocarbon fractions and risk indicators as required; incorporate an extraction method that is suitable for the weathered hydrocarbon range; be practical in application; and not entail excessive cost. We considered existing methods.

Soxhlet extraction is a widely used, benchmarked, exhaustive and easily-standardised technique for the extraction of petroleum hydrocarbon contaminated soils [The technique places a specialized piece of glassware in-between a flask and a condenser. The refluxing solvent repeatedly washes the solid extracting the desired compound into the flask.]. However, its disadvantages, including lengthy extraction times, degradation of thermally liable compounds, use of large volumes of organic solvents and the need to concentrate samples, have resulted in the investigation into alternative exhaustive and robust methods.

Ultrasonication is a quick, easy and cost-effective method that is now widely used in environmental analysis [he disintegration of soil structures (lysis) by means of ultrasound is used for the extraction of organic compounds of the soil].. However, analytical procedures using ultrasonication vary not only in the method used (eg type and volume of solvents, cycle duration etc), but also in the type of ultrasonic apparatus used (sonic probe or ultrasonic bath). Some of the more detailed investigations have shown that ultrasonic methods have the potential to produce equivalent or better efficiencies than currently used methods such as Soxhlet.

Conversely, other investigations have shown the opposite of this with worse efficiencies compared to current methods. We concluded that if sonication is to be used in place of traditional methods, it needs to be clearly defined and optimised.

A new ultrasonic method

As a result of the research, a novel solvent ultrasonic extraction procedure which allows petroleum hydrocarbon class fractionation and identification of risk-indicator compounds was developed by consortium partner TES Bretby, and is proving a competitive market technique. The method has been published in *Analytical chemistry Journal* and is available at:

http://pubs.acs.org/doi/abs/10.1021/ac800698g The analytical schematic recommended for analysing soil contaminated with weathered hydrocarbons is shown in Figure 1.

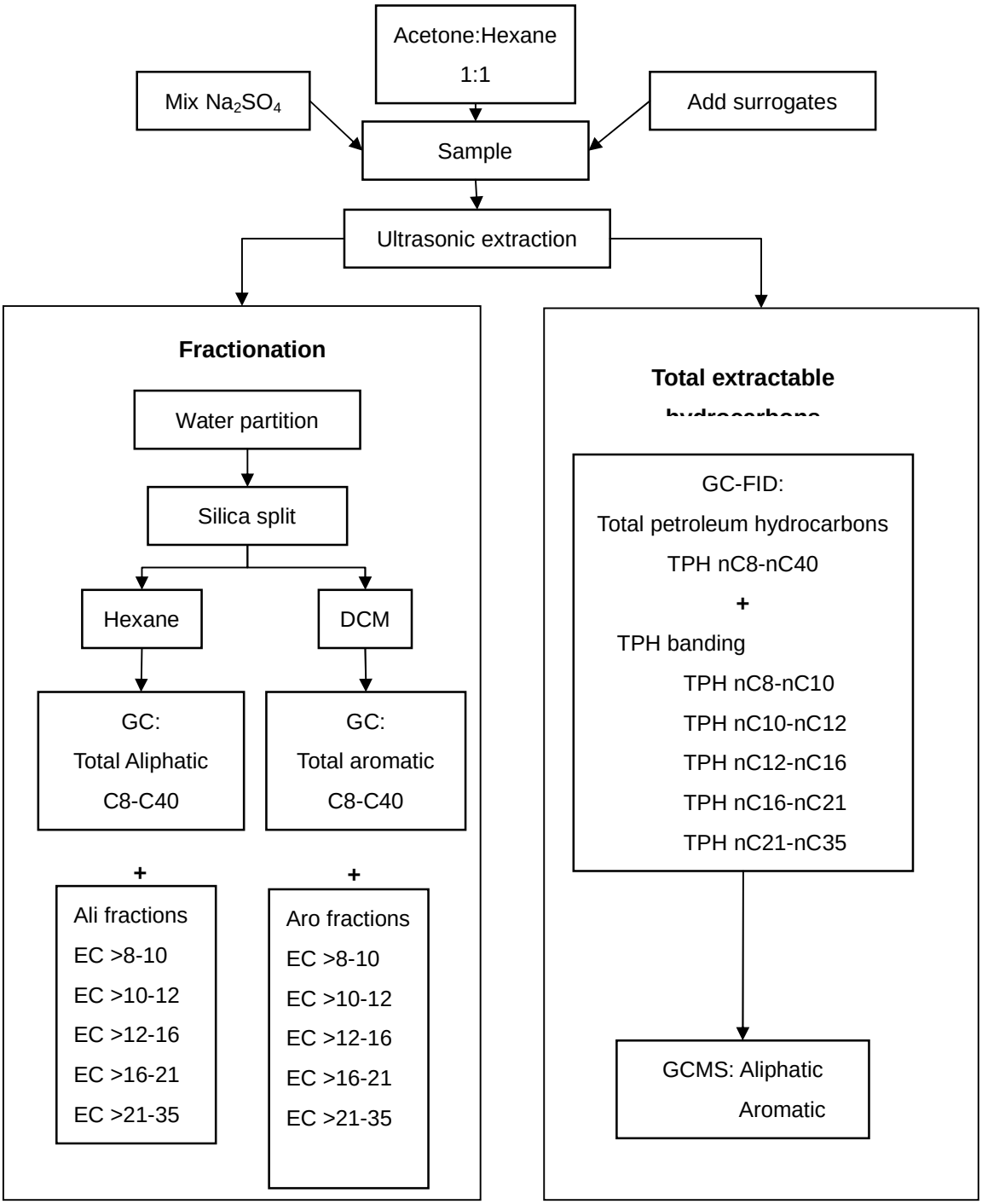

Figure 1: Analytical schematic for analysing soil contaminated with weathered hydrocarbons

The method covers the determination of total petroleum hydrocarbons (TPH) between nC8 and nC40, and sub-ranges of hydrocarbons including diesel range organic (DRO) compounds, kerosene range

organic (KRO) compounds and mineral oil range organic (MRO) compounds in soils. Further modifications to the TPH carbon banding may be made as requested for risk-assessment including ranges known as Texas Risk banding (TPH C8-C10, C10-C12, C12-C16, C16-C21 and C21-C35) as well as separation of the aliphatic and aromatic fractions as defined in the UK regulatory framework.

The method can be routinely used for measuring hydrocarbons down to 10 mg/kg in soil. With an extraction efficiency and recovery between 95–99%, this method can be easily positioned as a good alternative to Soxhlet extraction and shows a good potential for implementation as a standard method, potentially providing practical assistance to the contaminated land sector.

The method also conforms to the Environment Agency mCerts performance targets (30% bias, 15% precision) and is compatible with the existing UK risk framework.

We believe the technique is a vast improvement on conventional methods, as it saves time and lowers solvent consumption. Furthermore, there are no evaporation steps preventing the potential loss of front-end hydrocarbon bands and the use of water partitioning facilitates an effective solvent exchange prior to fractionation. There are fewer handling steps, and disposable apparatus eliminates potential cross contamination. Importantly, it is easy and simple to reproduce.

The company is already using the technique for site testing at the 2012 Olympic Park in London. While the direct effect of this work will take further time to assess, TES estimates an overall saving of £200k/y on its hydrocarbon analysis costs including:

* reduced use of solvents, saving £100k/y (especially due to reduced use of chlorinated solvents by 90%);

* improved laboratory throughput (four-fold faster than using previous methods): £80k/y ongoing) and;

* reduced quality control failures by either incomplete extraction of surrogates or cross contamination (£20k/y ongoing).

The method has been accredited ISO17025 for TPH analysis, banding and class separation and is currently under a validation process regarding precision issues for the mCERTs.

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